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## THE ENZYMATIC MEDIATED POLYMERIZATION OF PHENOL AND ANILINE DERIVATIVES ON A LANGMUIR TROUGH

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### ABSTRACT

Enzymatic polymerization of a number of monomers in an ordered lattice on a Langmuir trough (L-T) was investigated. The assembly and polymerization of two mixed monomeric systems consisting of 4-tetradecyloxyphenol (C14PP) with phenol, and 4-hexadecylaniline (C16PA) with aniline, in various ratios were carried out. Polymerization was obtained with C14PP and phenol (in the ratio 1:10), and C16PA and aniline (in the ratio 1:2) on buffered MilliQ water (pH 7.5) using the enzyme horseradish peroxidase (HRP) at 20°C. Polymerized monolayers were then transferred to appropriate substrates for UV-Vis, third order non linear optical (NLO) properties, and thickness measurements. Thermogravimetric analysis (TGA) was performed on the final polymers. Results suggest that the lattice controlled polymerization results in highly ordered conjugated polymers with improved functional, electronic, NLO and processability properties, which form a basis for intelligent materials design and applications.

### INTRODUCTION

Phenolic resins are one of the most studied polymeric materials because of the increased product demand ranging from commodity construction materials to high technology applications in electronics and aerospace. The starting materials for the production of these resins are phenols, or derivatized phenols, and aldehydes in the presence of a basic or acidic catalyst. However, since formaldehyde is a toxic chemical and potentially carcinogenic agent, production of the resins is strongly questioned from a safety standpoint.

A possible safe alternative is the use of biological enzymes for

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the coupling of phenols in the presence of hydrogen peroxide. The high specificity and catalytic rate of the enzyme minimizes the undesirable byproducts and simultaneously leads to the development of an environmentally friendly chemical process. This synthetic procedure in bulk solution was studied by Dordick et al. [1] and more recently by Akkara et al. [2]. They found that in dioxane/water systems, HRP catalyzes the polymerization of derivatized phenol and aniline compounds. The polymers exhibited good thermal stability and also interesting non linear optical (NLO) properties.

One major limitation of these polymer products is the difficulty found in the processing due to the presence of extensive crosslinking in the structure. To overcome this problem we employed enzymatic synthesis on a L-T. This approach significantly decreases the possibility of crosslinking, thereby improving the processability, while maintaining or even improving the electrical and third order NLO properties. This methodology was found to be applicable to various related compounds [3]. Here we report data on polymers formed by C14PP and phenol (1:10 ratio) and by C16PA and aniline (1:2 ratio). In particular, we characterized the two systems by pressure-area isotherms, TGA, and UV-Vis spectroscopy. Furthermore, for the C14PP/phenol we measured optical/electrical properties and thickness by means of ellipsometry and Atomic Force Microscopy (AFM).

## EXPERIMENTAL

A Lauda film balance equipped with a constant temperature bath (Langmuir Filmwaage, Model D, Lauda-Brinkman, Westbury, NY) was used. The surfactant C14PP was chemically synthesized by O-alkylation of hydroquinone with 1-bromotetradecane. C16PA was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Monomers at 1-2 mg/ml concentration were solubilized in chloroform and spread at the air-water interface. The monolayers were prepared at the air-water interface according to a published procedure [3]. The subphase contained two liters of 0.85 mM HEPES buffer, pH 7.5, with 12-25 mg of enzyme per liter. Powdered horseradish peroxidase (HRP) (EC 1.11.1.7), was preadded to the L-T subphase (Type II, 150-200 units/mg, Sigma Chemical Co., St. Louis, MO). Once the monomer at the air-water interface was spread onto the aqueous subphase containing HRP and compressed to 15 mN/m, hydrogen peroxide was injected into the subphase to commence the polymerization reaction.

Spectral characterization of monolayers on quartz slides was performed with a Perkin-Elmer Lambda-9 UV-Vis-Near IR spectrophotometer (Norwalk, CT). TGA measurements of the monomers and surface skimmed polymers were performed under nitrogen with a 10°C/min rate of temperature increase. A TGA 2950 from TA

Instrument Inc. (New Castle, DE) was used.

Five monolayers of C14PP/Phenol polymer deposited on fused silica (refractive index  $n=1.457$ ) were measured for thickness by ellipsometry using a Thin Film Ellipsometer (43603-200E, Rudolph Research, Flanders, NJ) at  $\lambda=0.6328 \mu\text{m}$ . One monolayer of C14PP/Phenol was deposited on a silica wafer for AFM using a Digital Instrument Inc NANOSCOPE AFM (Santa Barbara CA).

For electrical measurements, an "Interdigitated Microsensor Electrodes" (IME) was used. The IME was composed of fifty gold fingers, each  $15 \mu\text{m}$  wide,  $4985 \mu\text{m}$  long, and with a space of  $15 \mu\text{m}$  between each finger. This sensor was covered with bulk C14PP/phenol or C16PA/aniline polymer and then placed in a sealed chamber which was alternately flushed with nitrogen and evacuated three times, followed by resistance measurements of the undoped polymer. Nitrogen was gradually introduced along with dopant (iodine) into the chamber and electrical resistance was monitored. The measurement process was halted when saturation in conductivity resulted.

Third order non linear optical susceptibility ( $\chi^{(3)}$ ) was determined in solution by degenerate four wave mixing with a frequency doubled Nd:YAG laser with 17 ps pulses at 532 nm. The average energy per pulse was 25mJ. The vertically polarized output was split into three beams, which are temporally and spatially overlapped in the sample contained in a 1 or 2 mm cuvette. The intensity of the phase conjugate beam proportional to the square of  $\chi^{(3)}$  was measured.

## RESULTS AND DISCUSSION

Pressure-area isotherms with unreacted monomers C14PP and C16PA, and mixtures of these monomers with phenol and aniline are shown in Fig. 1. An area of approximately  $22 \text{ \AA}^2$  to  $25 \text{ \AA}^2$  per molecule was observed for the pure monomer systems. This increased area per molecule in comparison to the area per molecule of an alkyl chain ( $20 \text{ \AA}^2/\text{molecule}$  [4]) may be attributed to the presence of the phenyl group. The presence of the phenyl group imposes a disk-shaped benzene ring of maximum dimensions of  $7.4 \text{ \AA}$  across by  $3.4 \text{ \AA}$  thick and of minimum dimension of  $6.4 \text{ \AA}$  across by  $3.4 \text{ \AA}$  thick (the thickness of the  $\pi$ -cloud) on the alkyl chain. The calculated area of the phenyl group from molecular modeling ranges from  $21.8$  to  $25.2 \text{ \AA}^2$ . It is interesting to note that the introduction of the phenoxy group into the interior of the monolayer does not perturb the stability of the close packed monolayer shown by the C16PA isotherm which reaches a relatively high collapsed pressure of about  $70 \text{ mN/m}$ .

The expansion in area with added enzyme and underivatized phenol or aniline was encouraging because this indicates that these

components were permeating the monolayer. For reaction, underivatized phenol or aniline was added to the trough in ratios ranging from 1:1 to 500:1 (underivatized/derivatized). The reaction rate, upon injection of  $H_2O_2$ , was observed to increase as the ratio increased. UV-Vis spectroscopy characterizations (Fig.2) of the C16PA/aniline polymer multilayers exhibited a broad absorption in the visible spectrum, indicative of formation of a conjugated polymeric backbone structure. This absorption feature was absent in the controls containing only the monomer mixtures. Controls run in the absence of either hydrogen peroxide or HRP also gave no evidence of polymer formation. Collapsed polymerized films, skimmed from the subphase surface, were dark in appearance, and highly stretchable. Similar results were found for the C14PP/phenol system [5].

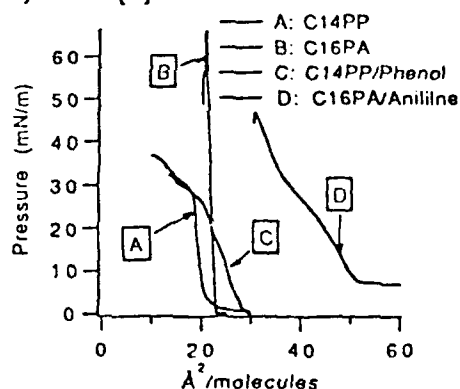


Figure 1. Isotherms of different monomers on MilliQ water (A,B), and in presence of HRP (C,D) at 20°C.

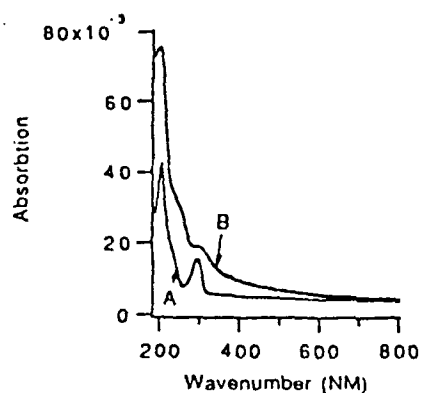


Figure 2. UV-Vis spectra of ten layers of C16PA/Aniline: (A) ten layers of the monomer, (B) ten layers of the polymer.

Thermal properties of the polymers were determined by TGA and are presented in Figure 3. The TGA analysis indicated that a significant amount of material remains after heating the polymer to 900°C. TGA of the C14PP/phenol polymer indicated about a 15% final residue value with two major temperature ranges of degradation; one between 250-400°C and the other between 400-470°C. Thermal analysis carried out for the C16PA/aniline polymer showed a 50% final residue value and similarly the presence of two different temperature ranges during the degradation process. The chemical and physical properties of this residual material have not been studied.

Optical ellipsometry is a way to measure the monomolecular thickness and quality of the films formed. By ellipsometry, we obtained a film thickness of  $27.8 \pm 1$  Å for the C14PP/phenol polymer. Our results are in reasonable agreement with the data (25 Å) obtained by modelling calculations. We employed a value of  $n_f = 1.50$  for the real refractive index of the film in the calculation of film

thickness. The use of this refractive index has precedent from previous investigations of monolayers [6], where values of 1.45-1.50 have been employed. The high end of this range was used, since the phenoxy and the phenyl group would be expected to increase the refractive index of the film, as can be seen by a comparison of the bulk refractive indices of tetradecane ( $n_D=1.4290$ ), anisole ( $n_D=1.5160$ ) and phenol ( $n_D=1.5509$ ). Thickness results were confirmed by AFM measurements where the micrograph showed a regular flat surface of 30 Å or lower thickness.

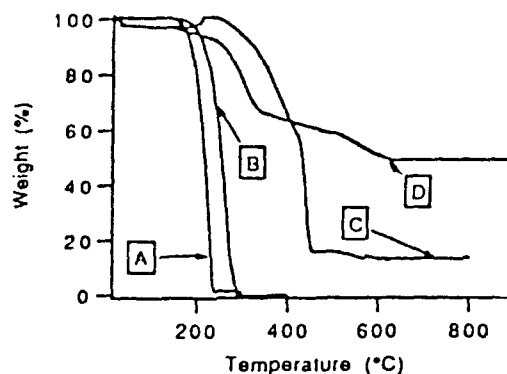


Figure 3. TGA of monomers (A) C14PP, (B) C16PA, and of polymers (C) C14PP/phenol (1:10), (D) C16PA/aniline (1:2).

Conductivity values of iodine doped polymerized multilayers of the C16PA/aniline (1:2) ranged from  $3 \cdot 10^{-3}$  to  $1 \cdot 10^{-5}$  S/cm. One such polymer sample was relatively stable and maintained a conductivity of  $2.00 \cdot 10^{-4}$  S/cm over a 3 day period after doping. The C14PP/phenol polymer showed similar behaviour [7] with a higher initial conductivity. There was also significant enhancement of the third order optical nonlinearities to values of  $1 \cdot 10^{-9}$  esu upon polymerization of the C14PP/phenol system. Such a result would be expected upon formation of a conjugated backbone structure.

A schematic of two possible arrangements of the polymerization products is given in figure 4.

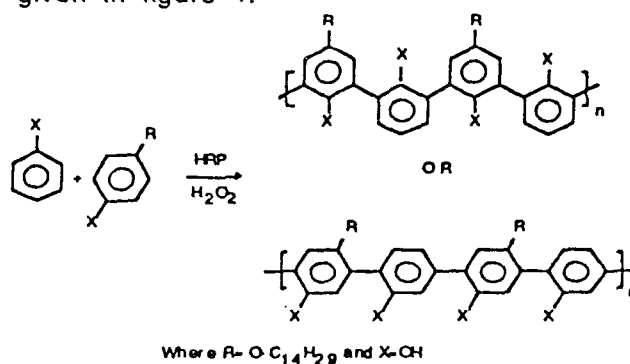


Figure 4. Schematic of two proposed polymer structures.



## CONCLUSION

The biocatalytic approach to 2-D polymeric synthesis we have described is a free radical polymerization process [8]. A wide range of monomers will react under these conditions to provide a diversity of potential polymeric products for systematic studies of the effect of monomer substituents on mechanical, thermal, electronic and linear/non linear optical properties [3]. The process described here represents a general technique for the assembly and polymerization of conductive and optically active polymers in 2-D networks. Processing limitations observed with intractable polymers synthesized in bulk are surmounted with this technique and thin films are formed as the reaction progresses.

## ACKNOWLEDGMENTS

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